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SMOKE COMPOSITIONS
BASED ON PHOSPHORUS

by

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MARCH, 1958

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3.] Smoke munitions.
4.] Phosphorus compounds—
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(FARNBOROUGH)

(SMOKE COMPOSITIONS BASED ON PHOSPHORUS)

by

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SUMMARY

A new slow burning smoke composition, developed for the Marker Marine No.4 Mk.1, is discussed against the background of the older phosphorus compositions. The chemical reaction on which it is based is shown to differ from that previously reported.

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1   INTRODUCTION

1.1   The purpose of this Note is to review the ways in which phosphorus can be used to produce smoke and flame, and against this background to record and discuss the work done on a new slow burning composition developed for the Marker Marine No.4 Mk.1.   Although further experimental work would be necessary to clarify all points, sufficient has been done to determine the course of the main reaction with reasonable certainty, and to show that it is different from that previously supposed.

1.2   Phosphorus is the most efficient smoke producing agent[1], and it has the advantage of giving flame with the smoke.   In burning, it combines with the oxygen in the air, and subsequently with the moisture, giving a dense white smoke containing oxides and acids of phosphorus which weigh over three times as much as the phosphorus from which they are produced.   The temperature of the smoke is initially high, and, except in strong winds, it "pillars", rising well clear of the ground or sea.

1.3   For producing smoke, phosphorus can be used in three ways:

(a)   as white phosphorus, which burns spontaneously on exposure to the atmosphere,

(b)   in combination with metals to form phosphides, which react with water to evolve phosphine, and other hydrides of phosphorus; these can be burned in the air to give the same white smoke,

(c)   as the allotropic, comparatively inert, form of red phosphorus, which can be boiled off from fuel/oxidant heater mixtures.   This phosphorus vapour ignites spontaneously on contact with the air.

1.4   The chemical reactions involved are in most cases complex; many side reactions are possible and some undoubtedly occur.   It is useful however to indicate the main course of each reaction, and convenient to compare the potential efficiencies of the various compositions in terms of the phosphoric acid which they can theoretically produce.   It is not implied that the smoke in all cases consists entirely of phosphoric acid (See Table 1).

2   WHITE PHOSPHORUS

2.1   The burning of white phosphorus is difficult to control and its rate is very dependent on the temperature, and on the amount of surface exposed to the air.   It is not used by the R.A.F. for marking, and its use in smoke shells and for smoke screening is almost obsolete; it finds some application for the ignition of incendiary fuel, as in the Fire Bomb.   Its main advantage is the absence of the need for an igniter.

2.2   The reactions can be expressed as follows:

$$P_4 + 5O_2 \rightarrow 2 P_2O_5 + 740 \text{ kcal.} \qquad (1)$$

$$P_2O_5 + 3H_2O \rightarrow 2 H_3PO_4 \text{ (phosphoric acid)} \qquad (2)$$
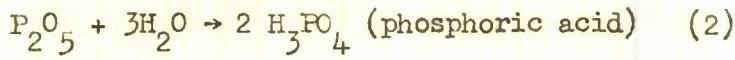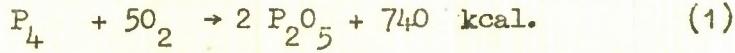
As the molecular weights of phosphorus and phosphoric acid are 124 and 98 respectively, it can be seen that each unit weight of phosphorus can give

$$\frac{4 \times 98}{124} = 3.16 \text{ units of phosphoric acid.}$$

3   METAL PHOSPHIDES

3.1   The phosphides of calcium, sodium, magnesium and aluminium have all been used in military stores for producing smoke and flame.

3.2   The ability of compounds of calcium and phosphorus to react with water and produce phosphine, has been known[2] since 1792.   Calcium phosphide was recognised[3] in 1861, and has been produced commercially since about 1920.   It was the first phosphide to be used in a service sea marker - the Flame Float, Aircraft, Navigation No.2 Mk.1, which emits smoke and flame for six minutes.   The rate of access of water is controlled by wire gauze and by the back pressure of the gas produced.   The chemical reactions are complex, but the main reaction is as follows:

$$Ca_3P_2 + 3 H_2O \rightarrow Ca(OH)_2 + 2 PH_3 \qquad (3)$$
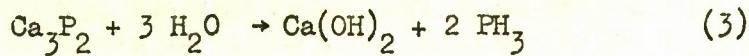
and the phosphine burns on contact with air as follows:

$$2 PH_3 + 4O_2 \rightarrow P_2O_5 + 3 H_2O \qquad (4)$$
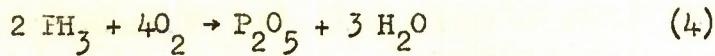
and the phosphorus pentoxide reacts with water, as shown in equation (2), to form phosphoric acid.

Summarising equations (3), (4) and (2)

$$Ca_3P_2 \rightarrow 2 H_3PO_4$$
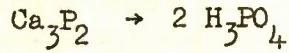
As the molecular weight of calcium phosphide is 182, each unit weight can give $\dfrac{98 \times 2}{182}$ = 1.08 units of phosphoric acid.

3.2   The phosphine produced by ordinary commercial calcium phosphide ignites spontaneously on contact with air, but this is due to the presence of an impurity, P_2H_4.   Calcium phosphide which has been heated to a high temperature does not produce this impurity[5] and the phosphine produced from it is not spontaneously inflammable.   A considerable volume of hydrogen (10 to 15%) is also produced by the reaction; this will add a little to the intensity of the flame, but on burning will only produce steam to give a temporary supplement to the volume of the smoke.

3.3   Sodium phosphide reacts with water much more vigorously than does calcium phosphide, and the phosphine produced burns with a yellow flame. It is used on the Flame Float, Aircraft, Navigation No.3 Mk.2, which burns for five minutes.

$$Na_3P + 3H_2O \rightarrow 3 NaOH + PH_3 \qquad (5)$$
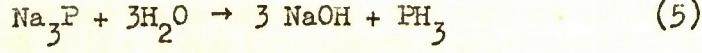
The phosphine reacts as shown in equation (4) and (2) so that

$$Na_3P \rightarrow H_3PO_4$$
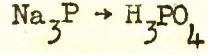
As the molecular weight of sodium phosphide is 100, each unit weight can give $\dfrac{98}{100}$ = 0.98 units of phosphoric acid.

3.4   In an attempt to improve the efficiency of phosphide filled markers, Messrs. Albright and Wilson suggested the use of the phosphides of polyvalent metals of lower atomic weight than calcium.   The phosphides of (a) magnesium and (b) aluminium were prepared and found to react with water, the main reactions being represented as follows

$$\text{(a)} \qquad Mg_3P_2 + 6\ H_2O \rightarrow 3\ Mg(OH)_2 + 2\ PH_3 \qquad\qquad (6)$$

so that

$$Mg_3P_2 \rightarrow 2\ H_3PO_4.$$
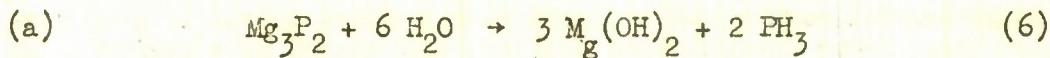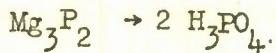
As the molecular weight of magnesium phosphide is 135, each unit weight can give $\dfrac{98 \times 2}{135} = 1.45$ units of phosphoric acid.

(b) Aluminium and phosphorus have been reported[5] to give a series of compounds: Al_3P; Al_5P; AlP and Al_2P_7, but the commercial product consists mainly of AlP which reacts with water as follows:

$$2\ AlP + 3\ H_2O \rightarrow Al_2(OH)_3 + 2\ PH_3 \qquad\qquad (7)$$

so that

$$AlP \rightarrow H_3PO_4$$
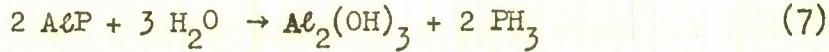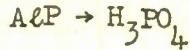
As the molecular weight of aluminium phosphide is 58, each unit weight can give $\dfrac{98}{58} = 1.69$ units of phosphoric acid.

Both magnesium and aluminium phosphides are therefore potentially more efficient than either calcium or sodium phosphide.   Aluminium phosphide is both difficult to manufacture and slow to react with water, whilst magnesium phosphide is relatively easy to prepare, and reacts with water at an inconveniently rapid rate.   The filling chosen for the Marker, Marine No.2 Mk.1 was the mixed phosphide produced by heating equal parts of magnesium and aluminium powders with phosphorus.   This is not difficult to prepare, and it reacts with water at a convenient rate to obtain the required functioning time of two hours.

3.5   The phosphine evolved by this mixed phosphide is not spontaneously inflammable at normal temperatures, and although some calcium phosphide is used to give initial ignition, the marker may not re-ignite if subsequently extinguished.

It was known that the admixture of oxides of nitrogen rendered the phosphine spontaneously inflammable, and a small generator containing sodium nitrite and potassium bisulphate was incorporated in the marker (Fig.1). On the admission of water these substances react as follows:

$$2\ NaNO_2 + 2\ KHSO_4 \rightarrow K_2SO_4 + Na_2SO_4 + H_2O + NO_2 + NO \qquad (8)$$
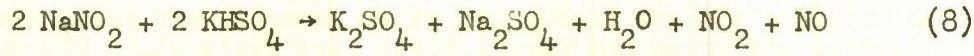
most of the nitrogen peroxide (NO_2) dissolves in the water, and the nitric oxide (NO) is evolved, and mixes with the phosphine near the emission orifice.

For spontaneous ignition at normal temperature, it is necessary to maintain the percentage of nitric oxide in the phosphine between 0.1 and 1.0. In practice it is found difficult to control the rates of emission of the two gases, to maintain the required ratio, and the marker tends to be unreliable in operation.

3.6 Phosphine ignites readily in air if its temperature is raised, and an experimental marker was produced with a short spiral of platinum wire, placed just above the emission orifice, and heated by a sea cell in the base of the marker. This proved effective in the limited tests given to it, but development was discontinued on the adoption of the red phosphorus compositions.

3.7 The phosphides provide a convenient means of obtaining a long functioning time, but their performance is difficult to control. Their initial performance falls quickly as shown in Fig.3, and the emission tends to continue at a low level long after the end of their normal functioning time. This slowing down of the rate of emission of phosphine is caused by the accumulation of reaction products within the marker; it is not liked by the service, as such dying markers may drift from the location being marked, and be confused with those more recently laid.

4   RED PHOSPHORUS COMPOSITIONS

4.1 Red phosphorus is produced commercially in the form of a powder with particles lightly coated with mineral oil, and in this form it is safe and convenient to handle. It is used in compositions of two types, in which the heat to vaporise the phosphorus is obtained by:-

(a)   the reaction of oxidants with fuels other than phosphorus,

(b)   the reaction of calcium sulphate (acting as an oxidant) with part of the phosphorus in the mixture.

The latter compositions are rather less efficient, but the system is simpler, and it is easier to study the interesting reactions which take place. The slowest burning compositions are of this type, but there is no reason to believe that equally slow compositions using fuels other than phosphorus, could not be developed.

4.2 The first red phosphorus smoke composition was produced in the U.S.A. for use in drift signals (see Table 2). Manganese dioxide (MnO_2) is the oxidant, with magnesium and calcium silicide probably acting as the main fuels. The weight loss on burning has been observed to be about 62%, but the maximum loss of phosphorus cannot exceed 55%, and the composition cannot therefore give more than:-

$$0.55 \times 3.16 = 1.74 \text{ times its weight of phosphoric acid}$$

(see para.2.2).

4.3 As this composition proved successful for short burning markers, C.S.A.R. (now A.R.D.E.) was asked to approve its use in British stores. Zinc oxide was not liked, and other changes were made, resulting in the development of composition S.R.414 (see Table 2). The phosphorus content is greater than that in the American composition and if all is volatilised, the composition can give

$$0.6 \times 3.16 = 1.89 \text{ times its weight of phosphoric acid.}$$

In practice the weight loss is lower (about 48%), and if this is all assumed

to be phosphorus the yield can be

$$0.48 \times 3.16 = 1.52 \text{ times its weight of phosphoric acid.}$$

Unlike the American composition, S.R. 414 suffers from the disadvantage of being easily extinguished by the entry of water through the marker orifice. It was nevertheless accepted for the Float, Smoke and Flame, $3\frac{1}{2}$ lb, Mk.1, and later for the Anti-submarine Training Indicator which was based on it.

4.4   The evolution of the hot (boiling point 287°C) and easily condensible (latent heat of vaporisation 209 calories per gramme) phosphorus vapour demands heat insulation to prevent its condensation within the marker.   This is achieved in the Anti-submarine Training Indicator (and in the Marker, Marine No.4 Mk.1), by an annular space between the candle case and marker wall, and by the use of a cone, sealed to the candle mouth, leading the vapour to the emission orifice without contact with the cold walls of the float chamber (see Fig.2).

4.5   To meet the requirement of a new marine marker (AW 215/OR 1107) to replace the unreliable No.2 Mk.1, a search was made for a filling which would burn at a slower rate than S.R.414.   If slow enough, such a composition would permit the use of a single short candle, almost the full diameter of the store, thus simplifying the operation of filling, and ensuring that the marker would remain upright in the water for most of its useful life. Messrs. Albright and Wilson were given a contract for the development of the filling, and called attention to the possibilities of the reaction between phosphorus and calcium sulphate reported by Berger[6] in 1920

$$5 \text{ CaSO}_4 + 2 \text{ P}_4 \rightarrow 5 \text{ CaS} + 4 \text{ P}_2\text{O}_5 + 269.3 \text{ Kcal} \qquad (9)$$
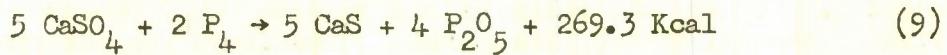
i.e. $$\frac{269.3}{5} = 53.9 \text{ Kcal per mole of CaSO}_4$$

If a limited excess of phosphorus is used, the heat of the reaction vaporised it, to be emitted and burn to give smoke and flame.   Using the compositions S.R. 622A, B and C, shown in Table 2, 10 lb of filling gave a burning time of 50 to 60 minutes, which was accepted for No.4 marker.

4.6   The compositions are rather difficult to ignite and a large flat pellet consisting mainly of composition S.R. 251 was found necessary for reliable ignition (see Fig.2).

The reaction between calcium sulphate and phosphorus takes place at a much lower temperature than that of most pyrotechnic mixtures.   (800°C has been recorded in the No.4 marker (see Fig.7), but the figure is likely to vary with the phosphorus content).   It is interesting in that it appears to depend on a balance between the heat generated by the reaction, and that required to vaporise the excess phosphorus, and compensate for heat losses due to radiation.   If the heat available falls below that required to vaporise all the excess phosphorus, as may happen if too much phosphorus is present, or if the heat insulation is inadequate, the reaction ceases and the candle goes out.   In the No.4 marker, compositions containing more than about 58% of phosphorus do not continue to burn; near this critical percentage, burning is slow and irregular and the candle is easily extinguished by the entry of water.

4.7   It proved necessary to use compositions poorer in phosphorus for the initial period (when heat must be provided to raise the temperature of the system) and at the end (when almost the whole of the cylindrical surface of the candle is hot, and heat begins to be lost also through its base).

Different compositions (see Table 2) are required for the 5 in. marker burning for 70 minutes, as this has a longer narrow candle.

4.8   Calcium sulphate/phosphorus compositions are easily extinguished by the entry of water, as happens when the marker is submerged in heavy seas, and considerable effort was expended in the development of orifices and traps to prevent water reaching the composition.   Consideration was also given to the possibility of adding to the composition some substance which would decompose in heating, to give inert gas.   This would mix with the phosphorus vapour, lower its partial pressure, and reduce its tendency to condense.   It would also act mechanically in maintaining some pressure within the marker should condensation of phosphorus occur.

Ammonium sulphate was tried in the expectation that it would produce nitrogen, but it was ineffective.

Anhydrous oxalic acid was tried, and the addition of 3% was found to prevent extinction of the marker even on immersion for periods up to 3 minutes.   As anhydrous oxalic acid is difficult to prepare, the commercial hydrated acid was substituted, and was equally effective.   Its decomposition can be represented as follows

$$(COOH)_2 \cdot 2 H_2O \rightarrow CO_2 + CO + 3 H_2O \text{ (steam)} \qquad (10)$$
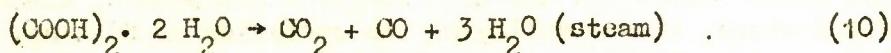
As the molecular weight of the hydrated acid is 126 and each mole of gas occupies 22.4 litres at N.T.P., it can be shown that the 0.3 lb present in the marker produces 9.8 ft^3 of gas and steam at 350°C.   To this must be added 1.9 ft^3 for the volume of the methane (CH_4) produced by the decomposition of the oil on the phosphorus.   Thus inert gas and steam are generated at the rate of about 0.23 ft^3/min over the functioning period of 50 minutes.

5   THE REACTION BETWEEN CALCIUM SULPHATE AND PHOSPHORUS

5.1   The No.4 marker contains 4.33 lb of calcium sulphate, 5.19 lb of red phosphorus and 0.3 lb of oxalic acid (see Table 3).   If the reaction proceeds according to Berger's equation (9), it can be shown that the maximum weight of phosphorus lost will be 3.7 lb, and it is unlikely that the acidic phosphorus pentoxide will volatilise in the presence of the basic calcium sulphide.   As the observed loss in weight of newly filled markers is 4.8 ±0.2 lb, it seems probable that the reaction may not be as represented by equation (9).

The following possible reactions were considered[7], and their heats of reaction calculated (Appendix 1) and expressed as kilocalories per mole of calcium sulphate at 25°C.

$$18\ CaSO_4 + 4\ P_4 \rightarrow 3\ Ca(PO_3)_2 + 5\ Ca_3P_2 + 18\ SO_3 \qquad -120.4 \text{ kcal.} \qquad (11)$$

$$18\ CaSO_4 + 5\ P_4 \rightarrow 6\ Ca(PO_3)_2 + 4\ Ca_3P_2 + 18\ SO_2 \qquad -53.5 \text{ "} \qquad (12)$$

$$30\ CaSO_4 + 7\ P_4 \rightarrow 5\ Ca_3P_2O_8 + 5\ Ca_3P_2 + 4\ P_2O_5 + 3\ SO_2 \qquad -43.1 \text{ "} \qquad (13)$$

$$42\ CaSO_4 + 7\ P_4 \rightarrow 9\ Ca_3P_2O_3 + 5\ Ca_3P_2 + 3\ SO_2 + 12\ SO_3 \qquad -42.0 \text{ "} \qquad (14)$$

$$6\ CaSO_4 + 3\ P_4 \rightarrow 3\ Ca(PO_3)_2 + Ca_3P_2 + P_4S_3 + 3\ SO_2 \qquad +1.7 \text{ "} \qquad (15)$$

$$18\ CaSO_4 + 5\ P_4 \rightarrow 6\ Ca_3P_2O_8 + 2\ P_4S_3 + 12\ SO_2 \qquad +31.0 \text{ "} \qquad (16)$$

$$4\ CaSO_4 + P_4 \rightarrow 2\ Ca(PO_3)_2 + CaS + SO_2 \qquad +40.3 \text{ "} \qquad (17)$$

$$9 \ CaSO_4 + 5 \ P_4 \rightarrow 6 \ Ca(PO_3)_2 + 3 \ CaS + 2 \ P_4S_3 \qquad +82.7 \ kcal. \qquad (18)$$

$$30 \ CaSO_4 + 19 \ P_4 \rightarrow 12 \ Ca(PO_3)_2 + 6 \ Ca_3P_2O_8 + 10 \ P_4S_3 \qquad +85.5 \ " \qquad (19)$$

$$30 \ CaSO_4 + 19 \ P_4 \rightarrow 6 \ Ca(PO_3)_2 + 12 \ Ca_2P_2O_7 + 10 \ P_4S_3 \qquad +90.3 \ " \qquad (20)$$

All give volatile compounds of sulphur, and sulphur dioxide can in fact be detected in the gases evolved from the No.4 marker. The more exothermic reactions are theoretically more probable, and it is seen that reactions (18), (19) and (20) give considerably more heat than the Berger reaction (9). Owing to the uncertainty of the thermo-chemical data, further evidence is necessary to decide which of these reactions takes place.

5.2   The presence of phosphorus sesquisulphide (P_4S_3) was confirmed in the effluent vapour, which on condensation gave a product in which the ratio of P_4S_3 to P was found to be 0.94 to 1. This is in reasonably good agreement with the ratio of 0.87 to 1 required by equations (19) and (20). X-ray analysis of the residue confirmed the presence of both calcium metaphosphate ($Ca(PO_3)_2$) and of calcium pyrophosphate ($Ca_2P_2O_7$). Calcium ortho-phosphate ($Ca_3P_2O_8$) was not detected and only traces of calcium sulphide (CaS) and calcium phosphide (Ca_3P_2) were found.

These observations confirm that the reaction (20) which is the most exothermic of those considered, is in fact the main reaction in the marker. Both the phosphates are present in their β crystal forms. $\beta - Ca(PO_3)_2$ is stated[7] to be stable between 500°C and 970°C, whilst $\beta - Ca_2P_2O_7$ is stated to be stable between 750°C and 1140°C. The presence of these forms is therefore consistent with the observed reaction temperature of 800°C.

5.3   Reaction (20) requires a weight loss from the marker of 5.39 lb (including an allowance of 0.37 lb for the loss of oil, oxalic acid, and gunpowder in the priming pellet). This is not in very good agreement with the observed loss (4.8 ±0.2 lb) but further work would be necessary to establish the reason for the difference. Such work is difficult and unpleasant as phosphorus vapour condenses to white phosphorus, which burns vigorously on exposure to the air when the marker is opened. Possible explanations for the smallness of the observed loss are:

(a)   incomplete burning of the composition – the weight of the unreacted composition which can be seen, never exceeds a few ounces;

(b)   condensation of P_4S_3 and P within the marker,

(c)   combination of phosphorus with the aluminium of the candle case and emission cone.

5.4   The P_4S_3 burns with the phosphorus vapour on emission, giving sulphur dioxide (SO_2 which can be smelled, but which makes no contribution to the smoke) and phosphorus pentoxide (P_2O_5).

$$P_4S_3 + 8 \ O_2 \rightarrow 3 \ SO_2 + 2 \ P_2O_5 \qquad (21)$$
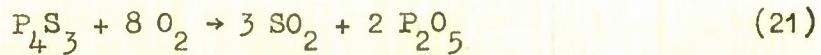
The maximum efficiency of the composition can be calculated on the basis of equation (20), and it can be shown that the total weight of phosphorus (free,

and combined as P_4S_3) which it can produce is 4.0 lb; the composition

can therefore produce $\dfrac{4 \times 3.16}{10} = 1.26$ times its weight of phosphoric

acid.   It is evident that the slow burning rate has been achieved at the cost of some loss in potential efficiency compared with S.R.414.

5.5   The performance of the No.4 marker has been compared with that of the No.3 Mk.2 (phosphide) marker by recording the light intensities of their flames over the functioning period (see Fig.3).   During most of the period of its burning the flame from the No.4 marker was at least three times as bright as that of the No.3 Mk.2 marker, and this observation is in fair agreement with the relative smoke densities observed on several occasions at sea[9].

The better performance of the No.4 marker is due to

(a) the increased charge weight (10 lb against 6 lb),

(b) the shorter functioning period (50 minutes against 2 hours),

(c) the completion of the reaction within the functioning period (see para.3.7).

6   THE HEAT BALANCE IN THE NO.4 MARKER

6.1   The heat produced during the burning of the marker can be calculated using the thermochemical data given in Appendix 1 and Tables 3 to 6.   On the assumption that the main reaction is represented by equation (20), the heat produced is calculated to be between 445 and 755 kcal (see Appendix 2). Of this heat, $255 + (0.227 \times 365) = 338$ kcal are required for heating the excess phosphorus from 10° to $375^{\circ}C$ and vaporising it (see Tables 4 and 5), leaving between 107 and 417 kcal for losses.

The heat lost to the air has not been measured, but is thought to be small, as the area exposed is not large.   The heat gained by the water in which the marker floats has been measured, and in two experiments 430 and 475 kcal were recorded.

The agreement with the higher calculated figure is reasonably good considering the difference between the observed and calculated losses in weight.   Condensation of phosphorus or phosphorus sesquisulphide within the marker would increase the heat available for radiation.

The observations are not inconsistent with the assumption that the main reaction is represented by equation (20) and it is evident that neither the Berger reaction nor those of low exothermicity represented by equations (11) to (17) could account satisfactorily for the amount of heat shown to be produced.

7   THE STABILITY OF CALCIUM SULPHATE/RED PHOSPHORUS COMPOSITIONS

7.1   It has been observed that the burning time of the No.4 marker increases slowly with age, and that this effect is accelerated by storage at elevated temperature.   The burning time increases by about 14% after two years storage in this country, and there is no evidence that the change is then complete[9].   The increase in burning time is accompanied by a decrease in average light intensity (Fig.4) and the total light output of the marker remains virtually unchanged.

Further work would be necessary to establish the cause of this change in burning time, and to find means of preventing it. Tests show that the prior addition of oil to the calcium sulphate causes an appreciable increase in the burning times of test candles (see Appendix 2), which leads to the belief that the change may be caused by the migration of oil from the red phosphorus to the calcium sulphate.

8   EFFECTS OF VARIATION IN THE COMPOSITION OF THE NO.4 MARKER (see Appendix 2)

8.1   The degree of consolidation has only a small effect; an increase in pressed density in the range 1.14 to 1.39 causes a small increase in burning time.

8.2   Inert impurities have a considerable affect on performance. If they replace either the phosphorus or the calcium sulphate, the balance between them is upset, and the burning time is changed accordingly. The addition of inert material (powdered silica) in amounts up to 10%. caused a marked increase in burning time of test candles in which the ratio of calcium sulphate to phosphorus remained constant; mixtures containing 15% silica failed to complete their burning. (see Fig.5).

8.3   The specific surface of the calcium sulphate influences the burning time. The burning time of test candles is decreased by about 7% by increase in specific surface from 7259 to 10,000 cm^2/g. The specification for composition S.R.622C allows adjustment of the ratio of calcium sulphate to phosphorus to allow for variation in specific surface. The calcium sulphate may be ground natural anhydrite or "dead burnt" gypsum.

8.4   The density of the calcium sulphate is thought to be important. One sample of high density failed to maintain reaction with red phosphorus; it contained about 6% impurity.

8.5   The percentage of oil on the red phosphorus has a marked effect on burning time. Burning time is decreased if it is omitted, and increased if it rises above the normal 1.25%. Test candles containing phosphorus with 1.75% and 2.25% oil failed to complete their burning.

8.6   The ratio of calcium sulphate to phosphorus is critical, and a small increase in the proportion of phosphorus causes a large increase in burning time (see Fig.5). The specification calls for an accuracy in weighing of $\pm\frac{1}{4}\%$ to ensure maintenance of the rate of burning within the required limits.

8.7   The effectiveness of mixing is not very important. The burning time of test candles decreased by about 10% by an increase in mixing time from 2 minutes to $3\frac{1}{2}$ hours. Mixing is carried out in a rectangular drum rotated about one of its diagonals.

9   CONCLUSIONS

(1)   A slow burning smoke composition has been developed with a potential efficiency rather less than that achieved for some of the faster burning compositions.

(2)   The tolerance to the ingress of water has been greatly improved by the addition of 3% of oxalic acid to the composition.

(3)   The long term stability of the composition requires further investigation.

(4)   The chemical reaction between calcium sulphate and phosphorus has been elucidated and shown to differ from that originally supposed.

(5)   On the basis of a few experimental measurements and some assumptions, the heat produced in the No.4 marker can be satisfactorily accounted for.

(6)   The fact that so much of the heat produced in the No.4 marker is lost by radiation, suggests that the efficiency of compositions containing red phosphorus might be increased considerably by improved lagging.   This may apply also to coloured smoke compositions, in which volatile dyestuff is similarly evaporated from a heater mixture.

10   ACKNOWLEDGEMENT

The author wishes to acknowledge the contribution made by the Research Staff of Messrs. Albright and Wilson Ltd., to the development of the compositions, and to the clarification of the chemical reaction between calcium sulphate and phosphorus.   They have carried out much of the experimental work recorded in this note.

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Ref. No.	Author	Title, etc.
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4	Anon	A.P. 1661E, 2nd edition, Section 1, Chapter 2.
5	Mellor, J. W.	A comprehensive treatise on inorganic and theoretical chemistry.
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7	Lowe and Topley	The chemical reaction involved in the burning of the pyrotechnic composition in the candle of Marker, Marine No.4 Mk.1. Albright and Wilson Tech. Report No.11.
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9	L. Ratcliff	The development of Marker, Marine No.4 Mk.1. R.A.E. Tech. Note No. Arm.619.

ATTACHED:

    Appendices 1 and 2

    Tables 1-6

    Drgs. Sk.Arm.47778-47784

    Detachable abstract cards

ADVANCE DISTRIBUTION:

    DA Arm
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    A Arm   4
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    Library
    Head of Arm Dept
    Head of Chemistry Dept
    Dr. A. N. Mosses   2

ATTACHED:

    Appendices 1 and 2

    Tables 1-6

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APPENDIX 1

CALCULATION OF THE HEAT OF REACTION, AND THE HEAT
BALANCE IN THE NO.4 MARKER

The heat given, or absorbed, by any chemical reaction is obtained by subtracting from the sum of the heats of formation of the reaction products, the sum of the heats of formation of the reactants. For each molecular species the number of molecules involved in the reaction is multiplied by its molecular heat of formation. This latter figure ($-\Delta H$) is usually given for a temperature of 25°C, and most of the figures in Tables 3 and 4 have been obtained from Ref.8. For the following phosphorus compounds, no figures are quoted in chemical literature, and those given have been calculated by Lowe and Topley[7].

	$-\Delta H$ (kcal per mole)
Calcium metaphosphate	588 ±15
Calcium pyrophosphate	799 ±15
Phosphorus sesquisulphide	20 ±5

For reactions occurring at temperatures above 25°C, the heat released will be diminished by that required to heat the reaction products to their appropriate temperature.

The figures in Tables 3 and 4 are applied to the three main reactions:

(a) main reaction between calcium sulphate and phosphorus

$$30 \; CaSO_4 + 19 \; P_4 \rightarrow 6 \; Ca(PO_3)_2 + 12 \; Ca_2P_2O_7 + 10 \; P_4S_3$$
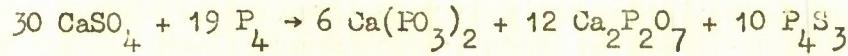
$$-[(30 \times 342.4) + (19 \times 17.6)] + (6 \times 588) + (12 \times 799) + (10 \times 20) = 2710 \; kcal$$

with an uncertainty of ±320 kcal. For each gramme molecule of calcium sulphate, the heat of reaction is $\frac{2710 \pm 320}{30} = 90.3 \pm 10.7$ kcal. As the No.4 marker contains 14.45 mole of calcium sulphate (see Table 3) the total heat produced by this reaction is 1305 ±155 kcal.

(b) decomposition of oxalic acid dihydrate

$$(COOH)_2 \cdot 2H_2O \rightarrow CO + CO_2 + 3 \; H_2O \; (Vapour)$$
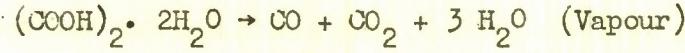
$$- 340.9 + 26.4 + 94.1 + (3 \times 57.8) = -47.0 \; kcal.$$

i.e. the reaction absorbs heat.

For the 1.08 mole present in the No.4 marker, the heat "produced" is 1.08 × -47.0 = -50.8 kcal.

(c) pyrolysis of the oil used to coat the phosphorus particles

$$2 \ C_{12} H_{26} \rightarrow 11 \ C + 13 \ CH_4$$
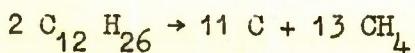
$$- (2 \times 87.5) + 0 + (13 \times 17.9) = 57.7 \text{ kcal}$$

i.e. $\dfrac{57.7}{2}$ = 28.85 kcal for each mole of oil.   For the 0.16 mole present in the marker the heat produced is 0.16 x 28.85 = 4.6 kcal.

(d) in addition to the heat produced by the above reactions, it is estimated[7] that the burning of the priming pellet produces about 17 kcal.

The total heat (calculated at 25°C) estimated to be produced by the composition in the No.4 marker is therefore the sum of these:

$$1305 \pm 155 - 50.8 + 4.6 + 17 = 1276 \pm 155 \text{ kcal}.$$

The heat produced at the temperature of functioning will be less than this by the heat required for the following:

(i)   heating the solid reaction products, and candle case assembly, to their observed temperature at the end of the functioning period (about 750°C - see Fig.7).

(ii) melting and vaporising the phosphorus sesquisulphide,

(iii) heating the gaseous reaction products to their emission temperature (about 375° - see Fig.8).

The heat absorbed in heating the solids is obtained by adding the products of their weights and specific heats (see Tables 4 & 6) and multiplying by the temperature rise - say 740°C i.e. from 10° to 750°C.

$$(0.510 + 0.195) \times 740 = 521.7 \text{ kcal.}$$

The heat required to melt and vaporise the phosphorus sesquisulphide is 81.5 kcal (see Table 5).

The heat absorbed in heating the gaseous reaction products is equal to the product of their heat capacity and temperature rise - say 365°C i.e. from 10°C to their emission temperature 375°C.   (see Table 4).

$$0.198 \times 365 = 72.3 \text{ kcal}$$

The heat produced by the reaction, and available for the evaporation of phosphorus, and for radiation, is therefore:

$$1276 \pm 155 - (521.7 + 81.5 + 72.3) = 600 \pm 155 \text{ kcal}.$$

APPENDIX 2

SOME EXPERIMENTAL OBSERVATIONS ON CALCIUM SULPHATE/PHOSPHORUS COMPOSITIONS

Unless otherwise stated all red phosphorus contains $1\frac{1}{4}\%$ of light mineral oil (Specification BS 148). It all passes through a 60 mesh sieve, and is to Specification CS 866. The calcium sulphate (Specification CS 2977) all passes through a 300 mesh sieve.

(1)   Effect of variation in the specific surface of calcium sulphate. $CaSO_4/P$: 47/53, burned in tin plate containers 3.87 in. diameter × 10.4 in. high.

Specific surface of $CaSO_4$ (cm^2/g)	Burning time (minutes)	Mean burning time (minutes)
10,700	33.63 32.83 31.75	32.7
7,250	35.25 35.66 34.50	35.1

(2)   Effect of addition of inert material (silica of the same degree of fineness as the calcium sulphate). 2920 g of composition burned in tin plate containers 39.4 in. diameter × 11.75 in. high.

$CaSO_4$ (%)	P (%)	Silica (%)	Burning time (minutes)
46	54	0	46.1
(95% 46 : 54)		5	53.7
(90% 46 : 54)		10	60.8
(85% 46 : 54)		15	(31.0 – $4\frac{1}{2}$ in. burnt)
46	52	2	43.7
46	50	4	41.6
46	48	6	37.4
45	54	1	53.0
44	54	2	60.0
43	54	3	68.3
42	54	4	77.2

/Table

(3) Effect of oil, on phosphorus and on calcium sulphate. Compositions burned in tin plate containers.

CaSO$_4$ (%)	P (oiled) (%)	Oil on CaSO$_4$ (%)	Oil on P (%)	Burning time (minutes)	Mean burning rate (sec/in.)
46	54	0	$1\frac{1}{4}$	42.5; 42.8	218
46	54	1	$1\frac{1}{4}$	55.0	280
46	54	0	$2\frac{1}{4}$	19.0*; 32.0*	233
48	52	0	0	21.2	109
48	52	$1\frac{1}{4}$	0	20.5	105
48	52	0	$1\frac{1}{4}$	28.3	144
48	52	1	$1\frac{1}{4}$	32.9	168
48	52	0	$1\frac{1}{4}$	21.5*	152
48	52	0	$2\frac{1}{4}$	18.0*	–

* failed to burn completely.

(4) Effect of mixing time. CaSO$_4$/P : 47/53, mixed in eccentrically mounted rectangular drum rotated at 23 R.P.M., burned in tin plate containers 3.87 in. diameter × 10.4 in. high.

Mixing time (minutes)	Burning time (minutes)
2	36.2
5	35.6
15	35.2
60	34.8
210	33.6

(5) Effect of degree of consolidation. Compositions burned in tin containers.

CaSO$_4$ (%)	P (%)	Dia. of container (in.)	Density (g/c.c)	Burning rate (sec/in.)
47	53	3.87	1.24	198
			1.32	201
			1.36	192
			1.39	187
46	54	3.16	1.14	224
			1.19	225
			1.24	223
			1.31	220
			1.37	220

TABLE 1

Potential smoke producing efficiencies of phosphorus compounds and compositions

Compound or Composition	Phosphorus %	Theoretical weight of Phosphoric acid produced per unit weight of composition
White phosphorus	100	3.16
Sodium phosphide	31.0	0.98
Calcium phosphide	34.2	1.08
Magnesium phosphide	46.3	1.45
Aluminium phosphide	53.4	1.69
U.S. Drift Signal composition	55.0	1.74
S.R. 414	60.0	1.89
S.R. 622A, B and C in No.4 marker	51.9	1.26

TABLE 2

Compositions based on red phosphorus

Material	U.S. Drift Signal (1 lb)	Float, Smoke and Flame 3½ lb S.R. 414 (0.66 lb)	S.R. 622 (0.66 lb)	5 in. Marine Marker					
				10 minutes (10 lb)	50 minutes S.R.622A (2 lb)	S.R.622C (6 lb)	S.R.622B (2 lb)	70 minutes "A" (2 lb)	"B" (8 lb)
Red phosphorus (oiled)	50 + 5	60	46	41	48.0	55.0	52.0	50.5	55.5
Calcium silicide	3.0	6							
Magnesium	7.5	6							
Manganese dioxide	34.0	28							
Zinc oxide	3.0								
Boiled linseed oil	3.0								
Calcium sulphate			51	55	49.1	42.1	45.1	46.5	41.5
Oxalic acid dihydrate			3	3	2.9	2.9	2.9	3.0	3.0
Burning rate sec/in.	75-80	75-80	75-80	40	220			200	
% loss on burning	62	48			48 ± 2				

Technical Note No. Arm.617

TABLE 3

Materials initially present in the composition of the No.4 marker

Constituent	Formula	A		B		B/A
		Molecular weight	Molecular heat of formation $-\Delta H$ kcal	Amount present		
				lb	gramme	mole
Red phosphorus	P_4	124	17.6	5.19	2360	19.05
Calcium sulphate (anh.)	$CaSO_4$	136	342.4	4.33	1965	14.45
Oxalic acid dihydrate	$(COOH)_2 \cdot 2 H_2O$	126	340.9	0.30	136	1.08
Oil (coating phosphorus)	$C_{12} H_{26}$	170	87.5	0.06	27	0.16
Impurities	–	–	–	0.12	54	–
TOTALS				10.00	4,542	

TABLE 4

Reaction products of the No.4 marker

State	Substance	Formula	A Molecular weight	Molecular heat of formation -ΔH kcal	B Specific heat cal/g/°C	C Amount present lb	C Amount present gramme	C/A mole	B x C/1000 Heat capacity kcal per 1°C temp. rise
SOLID	Calcium metaphosphate	$Ca(PO_3)_2$	198	588	0.25	1.261	571	2.89	0.143
	Calcium pyrophosphate	$Ca_2P_2O_7$	254	799	0.24	3.234	1465	5.78	0.352
	Carbon	C	12	0	0.22	0.023	10	0.87	0.002
	Impurities	-	-	-	(0.24)	0.120	54	-	0.013
	TOTAL					4.638	2100	-	0.510
GASEOUS	Phosphorus sesqui-sulphide	P_4S_3	220	20.0	0.15	2.335	1066	4.85	0.160
	Methane	CH_4	16	17.9	0.50	0.037	17	1.05	0.008
	Carbon monoxide	CO	28	26.4	0.16	0.067	31	1.08	0.005
	Carbon dioxide	CO_2	44	94.1	0.16	0.105	48	1.08	0.008
	Water vapour	H_2O	18	57.8	0.30	0.128	58	3.24	0.017
	TOTAL					2.672	1220		0.198
	Phosphorus vapour	P_4	124	17.6	0.186*	2.689	1220	9.84	0.227

* Taken as the mean of specific heats of 0.215 for the solid and 0.156 for the vapour

TABLE 5

Heat required to vaporise phosphorus and phosphorus sesquisulphide

Substance	Change of state	A Latent heat cal/g	B Amount present in reaction products gramme	A x B/1000 Heat required for vaporisation kcal
Phosphorus	sublimation	209.0	1220	255
Phosphorus sesquisulphide	(fusion (evaporation	9.1 67.4	1066	81.5

TABLE 6

Metal components which absorb heat (No.4 marker)

Component	Material	A Specific heat cal/g/°C	B Weight lb	B Weight gramme	A x B/1000 Heat capacity kcal per 1°C temp. rise
Candle case	Aluminium	0.24	0.96	436	
Candle closing plate			0.31	142	
Cone			0.43	194	
TOTAL			1.70	772	0.186
Perforated central tube	Steel	0.13	0.12	53	
Pellet holder			0.04	16	
TOTAL			0.16	69	0.009
TOTALS for metal components			1.86	841	0.195

MAIN OUTLET TUBE

TAIL

BUOYANCY CHAMBER

PILOT OUTLET TUBE

SODIUM
NITRITE

OPEN MESH
CYLINDER

DIAPHRAGM

BRASS
TUBE

FLANNEL
SHEATH

SPRING SUPPORTING
PLATE

SPRING

POTASSIUM
BISULPHATE

CYLINDRICAL
GAUZE BAG

SECTION ON A-A

SPRING
GAUZE WASHER
BRASS CAP

GAUZE COVERED
PLATE

GLASS WOOL

CALCIUM PHOSPHIDE

GLASS CLOTH
MAGNESIUM-ALUMINIUM
PHOSPHIDE

SUSPENSION LUG

LOCATING PIECES

SUSPENSION BAND

OPEN-MESH
CYLINDER

WATER INLET TUBE

FLANNEL SHEATH

BODY

BRASS TUBE

FLANNEL WASHERS

HOLE

BRASS WASHER

VALVE BODY

GAUZE THIMBLE

CENTRAL HOLE

VALVE SPRING

NOSE

ADHESIVE TAPE

BAKELITE DISC

NOSE TRANSIT COVER

STOPPER

FIG.I SECTION THROUGH BODY
OF MARKER MARINE No 2 MK.I

EMISSION
ORIFICE
ASSEMBLY

PARACHUTE

SPUN
CLOSURE

FLOAT
CHAMBER

PERFORATED PLATE
FILTER.

METAL CONE

INSULATING
CONE

PRIMING
FILLET

L.T. FUZE

35.5 IN.

PRIMING
COMPOSITION

PERFORATED
CENTRAL
TUBE

RED
PHOSPHORUS
CALCIUM
SULPHATE
OXALIC ACID

SHEET METAL CASE
0.016 IN. THICK

BAKELISED PAPER
LINING (FOR
STRENGTH)

MAIN
COMPOSITION

INSULATING
CAVITY

SPACING
RING

BAKELISED PAPER
CYLINDER (FOR
HEAT INSULATION)

END
COMPOSITION

SEA CELL

TRANSIT CLIP

SEA ANCHOR

PRESS CAP LID

NOSE CAP

4.9 IN. DIA.

FIG. 2 MARKER, MARINE, No 4 MK. I

FIG. 3. REPRESENTATIVE LIGHT EMISSION
CURVES FOR MARINE MARKERS Nº 2 & Nº 4.
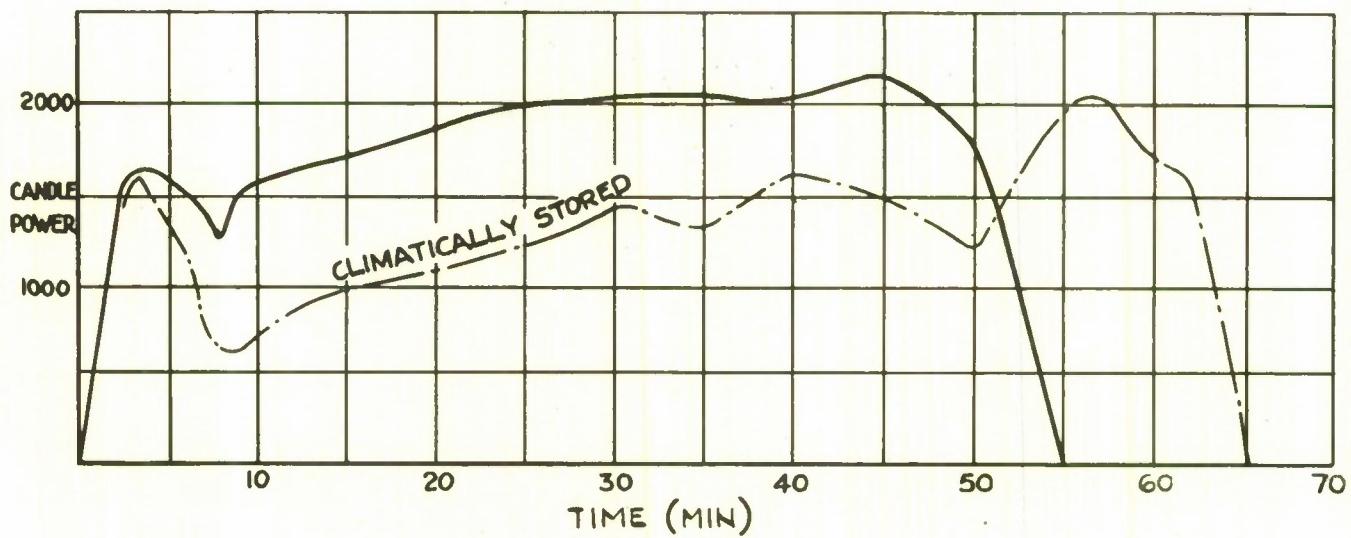
FIG.4. LIGHT EMISSIONS FROM Nº 4 MARKERS.
BEFORE AND AFTER CLIMATIC STORAGE.
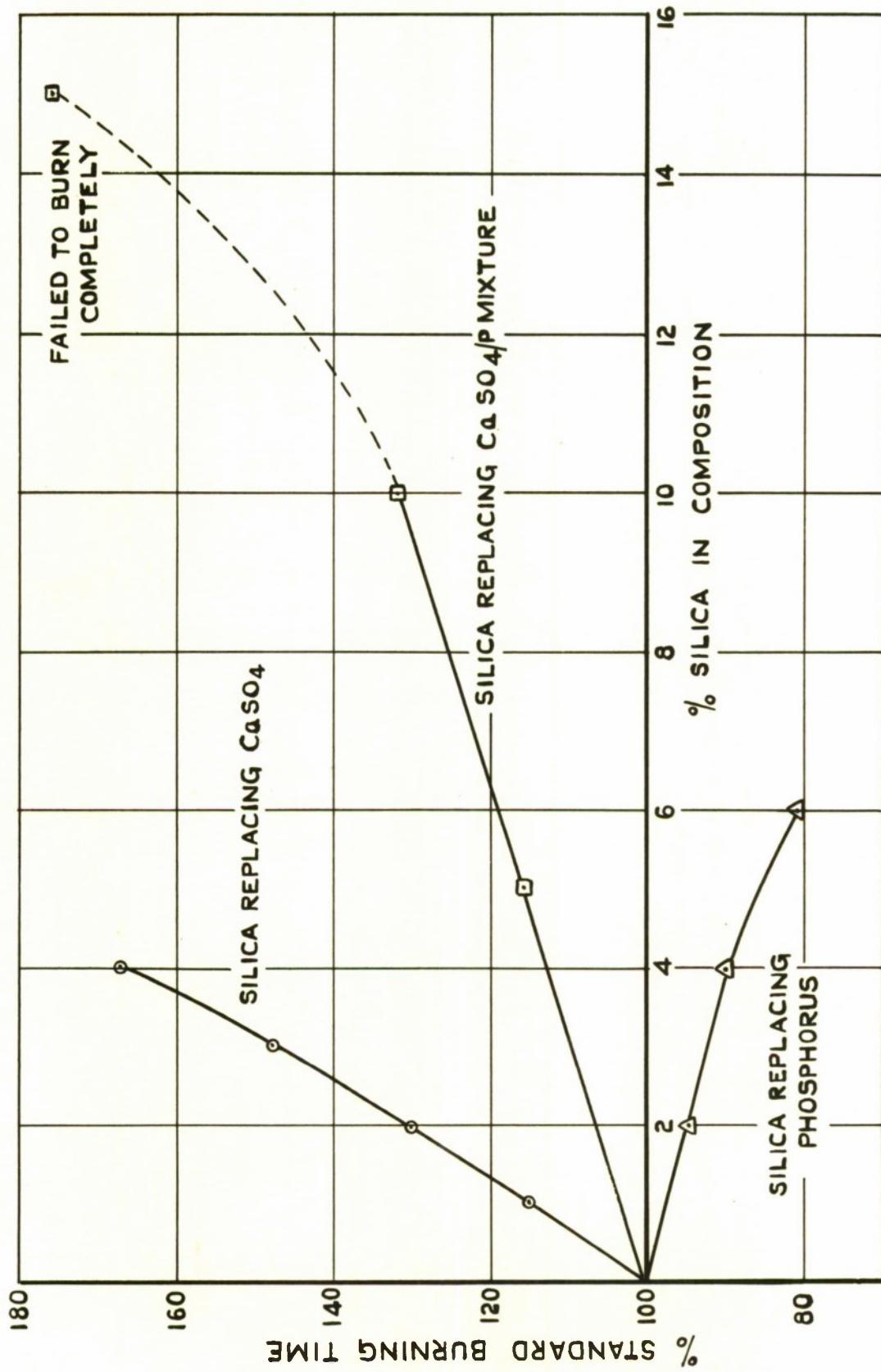
FIG.5 EFFECT OF IMPURITIES ON BURNING TIME OF
Ca SO₄ / P (46 : 54) IN TINPLATE CONTAINERS
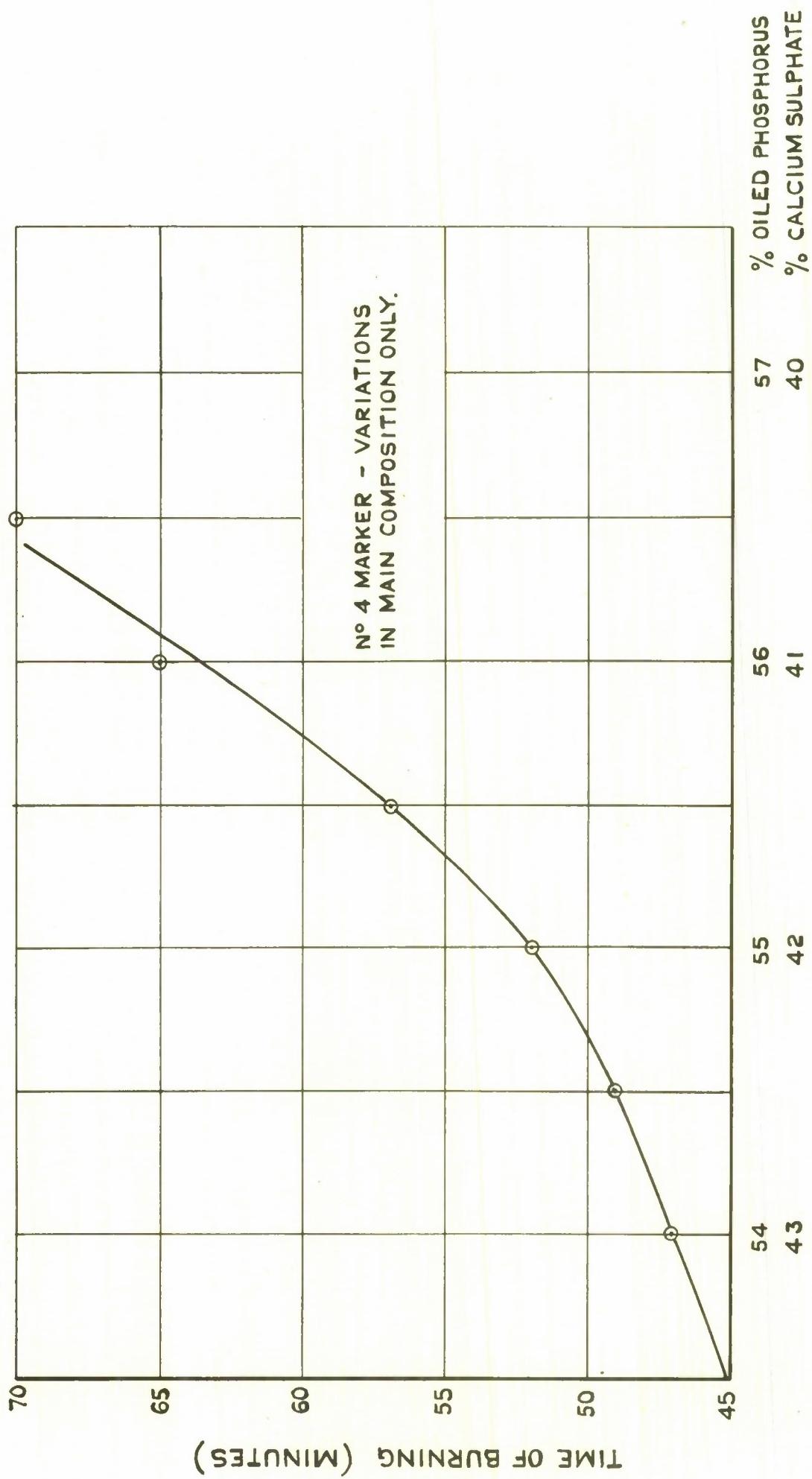
FIG.6 EFFECT OF COMPOSITION ON BURNING TIME

PLATINUM / PLATINUM RHODIUM
THERMO COUPLE PLACED
8 IN. FROM BASE OF CANDLE
1 IN. FROM OUTER SURFACE

TIME (MINUTES)
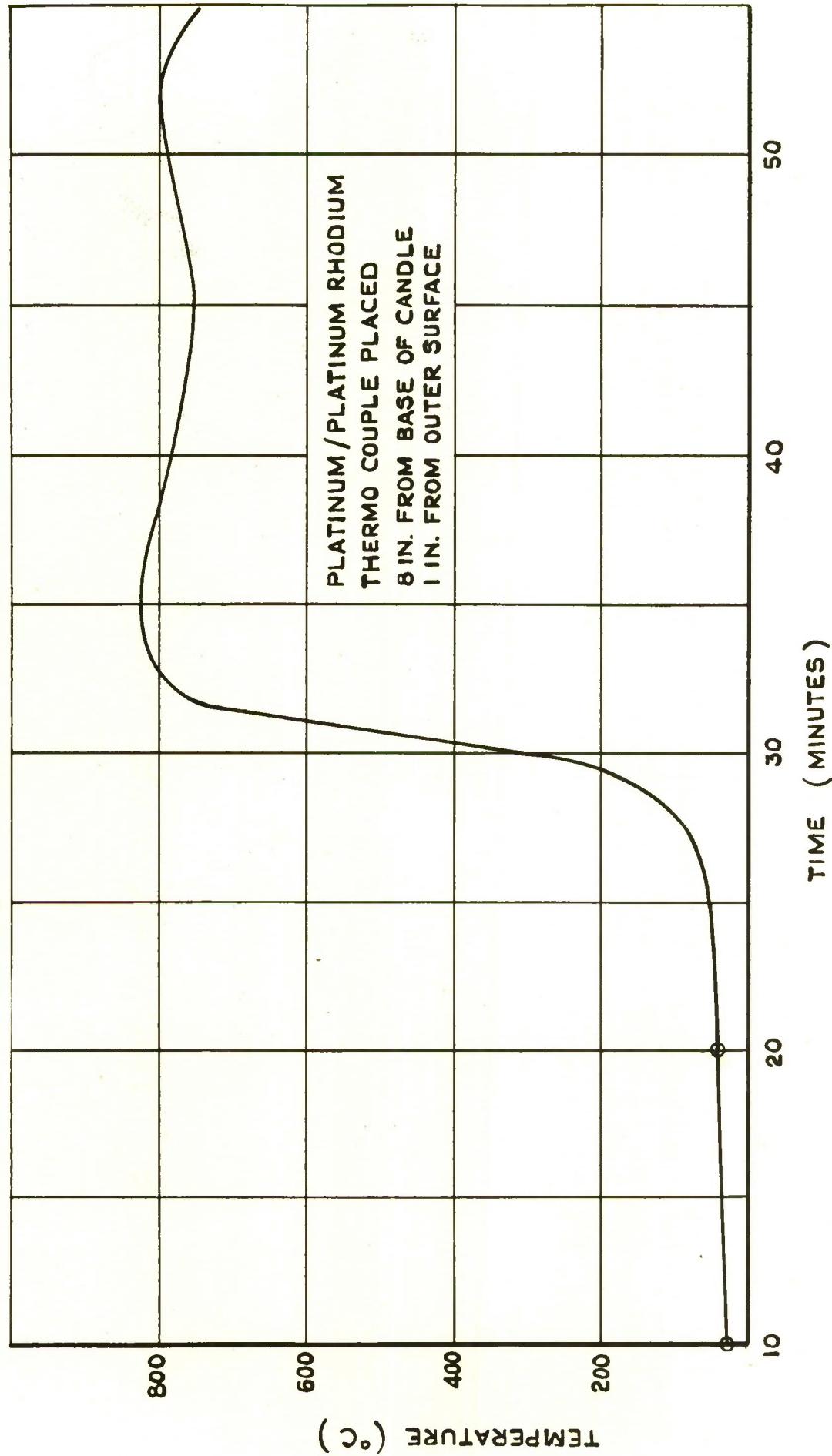
TEMPERATURE (°C)

FIG. 7 TEMPERATURE OF COMPOSITION IN No. 4 MARKER
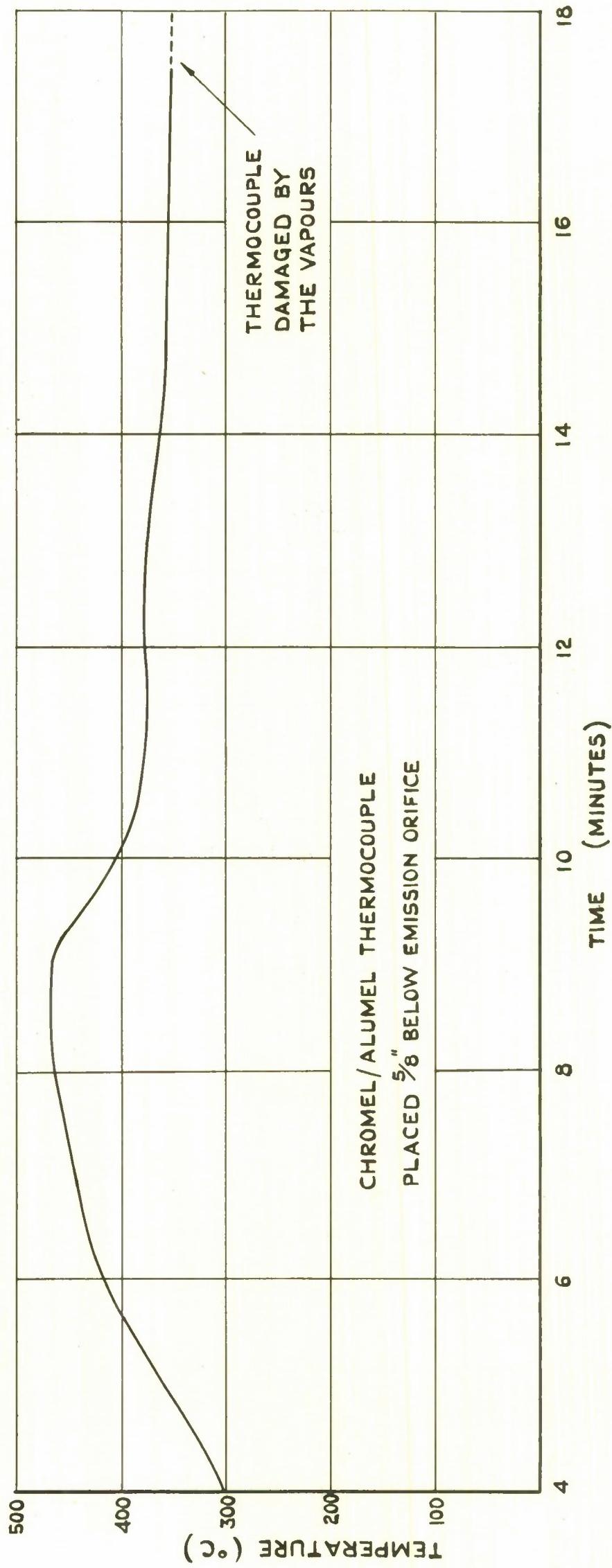
FIG. 8 TEMPERATURE OF VAPOURS IN No 4 MARKER

[dstl]

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